

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### New Organic Polyisocyanates and their Manufacture

We IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to organic polyisocyanates and to the manufacture thereof.

It has already been proposed to react diisocyanates with glycols and triols to form urethane polyisocyanates and to use such compounds as polyisocyanates in the manufacture of polyurethane products. The reaction between a diisocyanate and a glycol or triol according to the prior art stops at the stage at which all hydroxyl groups in the reaction mixture have been converted to urethane groups.

It has now been found that such urethane isocyanates may be reacted further with organic diisocyanates by using more forceful reaction conditions, involving the application of heat or the use of catalysts, or both, until substantially one molecule of diisocyanate has reacted with each urethane group present. The products of this reaction are essentially allophanate polyisocyanates of higher isocyanate functionality which because of their high solubility in organic solvents and in other polyisocyanates are useful in the manufacture of polyurethane products.

Thus according to the present invention there are provided new compositions of matter consisting essentially of allophanate polyisocyanates, which compositions are obtainable by reacting an amount in excess of

$n$  moles of an organic diisocyanate with one mole of a urethane isocyanate of the general formula  $R^1(OOCNHRNCO)_n$ , wherein  $R^1$  is a monovalent or polyvalent organic radical which is the residue of a mono- or polyhydroxylic compound after reaction of the hydroxyl groups with isocyanate groups,  $n$  is an integer from 1 to 6 and represents the functionality of the hydroxylic compound and  $R$  is a divalent substituted or unsubstituted organic radical, the reaction being carried out under conditions such that substantially one molecule of diisocyanate reacts with each urethane group present, as indicated by the measured isocyanate group content of the reaction mixture.

The divalent organic radical  $R$  in the general formula above may be alkyl, straight chain or branched, cycloalkyl, aryl or aralkyl and may be substituted for example by halogen, nitro or other radicals non-reactive to the isocyanate group.

Examples of suitable divalent organic radicals include aliphatic radicals such as tetramethylene and hexamethylene, cycloalkyl and substituted cycloalkyl radicals such as  $-C_6H_{10}-$ , aralkyl radicals such as  $-C_6H_4-CH_2-$  and  $-CH_2-C_6H_4-CH_2-$  and divalent aromatic radicals such as those derived from substituted or unsubstituted benzenes, diphenylmethanes, diphenyl ethers, diphenyls and naphthalenes.

Particularly preferred reaction products are those derived from urethane isocyanates wherein  $R$  represents a divalent radical derived from toluene, hexane, benzene, xylene or methyl cyclohexane.

The mono or polyvalent radical  $R^1$  in the general formula given above may be derived from any mono or polyhydric alcohol having from 1 to 6 hydroxyl groups by the removal of the hydroxyl group by reaction with an isocyanate group.

Examples of mono or polyhydric alcohols from which the radical  $R^1$  may be derived include among others methanol, ethanol, isopropanol, phenol, ethylene glycol, diethylene glycol, butane-1:4-diol, butene-1:4-diol, butyne-1:4-diol, hexane-1:6-diol, *z*:*z*'-p-xylylene diol, neopentyl glycol, glycerol, trimethylol propane, trimethylol ethane, pentaerythritol, monoallyl ethers of glycerol or trimethylol propane, mono or bis ethers of pentaerythritol, hydroxyl ended polyesters which may be linear or branched, and hydroxyl ended polymers and copolymers of cyclic oxides, for example ethylene oxide, propylene oxide, butylene oxide and tetrahydrofuran which may be prepared for example by the polymerisation of a cyclic oxide in the presence of a basic catalyst and optionally in the presence of a compound containing one or more active hydrogen atoms.

Preferred alcohols are those containing from 2 to 6 hydroxyl groups, e.g. ethylene glycol, diethylene glycol, trimethylol propane, glycerol, butylene glycols and products obtained by oxypropylation of diethylene glycol, trimethylolpropane and sorbitol.

Any organic diisocyanate may be used in the preparation of the products of the present invention. Examples of suitable diisocyanates include hexamethylene diisocyanate, tolylene-2:4 and 2:6-diisocyanates, diphenylmethane diisocyanate, 3-methyldiphenylmethane diisocyanate, *m*- and *p*-phenylene diisocyanates, xylylene diisocyanates, chlorophenylene - 2:4 - diisocyanate, naphthalene - 1:5 - diisocyanate, diphenyl - 4:4' - diisocyanate, 4:4' - diisocyanate - 3:3' - dimethyldiphenyl, diphenyl ether diisocyanates and dicyclohexylmethane diisocyanate. Mixtures of diisocyanates may be used.

Preferred diisocyanates are hexamethylene diisocyanate tolylene diisocyanates, methylcyclohexyl diisocyanates and xylylene diisocyanate.

The precise nature of the total composition produced according to the present invention has not been completely established, but from the close agreement between the isocyanate group contents of the products, as measured by methods well-known in the art, and the calculated theoretical values it is evident that they are essentially allophanate polyisocyanates produced by reaction of the urethane isocyanate with the organic diisocyanate in such a manner that each urethane group reacts with one molecule of diisocyanate.

As a further embodiment of the present invention there is provided a process for preparing the reaction products of the present invention by reaction of an excess of organic diisocyanate with a urethane isocyanate, as hereinbefore defined, optionally in the presence of a metal carboxylate, metal chelate or tertiary amine as catalyst.

As suitable catalysts for use in the process of the present invention there may be mentioned organic acid metal salts such as zinc, cobalt, iron, antimony, titanium, lead, calcium, bismuth, manganese, cadmium, thorium, zirconium or tin naphthates or octoates, complexes of the above metals with  $\beta$ -diketones such as acetyl acetone, organometal salts such as dibutyl tin dilaurate or tertiary amines such as triethylamine, pyrrolizidine, *N*:*N*-dimethyl phenylethylamine, *N*:*N*-dimethylcyclohexylamine, tetramethylethylene diamine, *N*-ethyl morpholine, 4-dimethylaminopyridine, triethylene diamine and tetramethylguanidine.

This process may be carried out over a wide range of temperatures; in the absence of a catalyst it is preferred that the reaction be carried out at a temperature of from 110°C. to 160°C. The addition of a catalyst to the reaction mixture permits the use of lower reaction temperatures, for example in the range 0°C. to 50°C.

The reaction is carried out using an excess of the organic diisocyanate as hereinbefore defined, the excess may vary over wide limits, it is preferred to use the organic diisocyanate in an excess of from 10% to 300% over that required for the reaction of one molecule of diisocyanate with each urethane group.

Any excess unreacted organic diisocyanate may be removed from the reaction product for example by extraction methods or by distillation methods such as distillation in a thin film distillation apparatus.

Any suitable organic diisocyanate may be employed in the present process. Examples of suitable diisocyanates are listed above.

Suitable urethane isocyanates of the general formula as hereinbefore defined for use in the present process may be prepared by methods well known in the art by the reaction of mono or polyhydric hydroxylic compounds and organic diisocyanates. Examples of polyhydric hydroxylic compounds include those given above from which the radical  $R^1$  may be derived. Examples of suitable diisocyanates include the diisocyanates listed above which may be used in making the new compositions of the present invention.

The urethane isocyanates may be prepared, isolated and then reacted with organic diisocyanate to form the novel compounds of the present invention or alternatively the polyhydric alcohol may be reacted with a convenient excess of the diisocyanate and without isolation of the urethane isocyanate the

product may be converted to a composition of the present invention for example by heating.

5 The process of the present invention may be carried out in the presence or absence of a solvent such as an ester solvent for example ethyl acetate or butyl acetate.

10 The new polyisocyanates of this invention may be used alone or in combination with other polyisocyanates for the manufacture of polyurethane products which may be homogeneous or cellular, rigid or flexible. The manufacture of such polyurethane products may be carried out by methods well known in the art. Polyurethane products which may be manufactured from the new polyisocyanate compositions include surface coatings, foamed cellular products, potting compounds and other polyurethane elastomers also adhesives for bonding metal to rubber and textiles to rubber.

15 The polyisocyanate compositions of the present invention, which after removal of excess organic diisocyanate do not present a volatile toxic hazard to the user are polyisocyanates of high functionality which possess adequate solubility in organic solvents and are especially useful in polyurethane coating compositions prepared for example by reaction of the products of this invention with polyol, polyamines or water in the form of atmospheric moisture and in the manufacture of rigid and flexible polyurethane foams.

20 The invention is illustrated but not limited by the following examples in which parts and percentages are by weight:

#### EXAMPLE 1

25 To 504 parts of hexamethylene diisocyanate maintained at 70°—75°C. is added over 30 minutes with stirring 53 parts of diethylene glycol. After completion of the addition the mixture is stirred a further 30 minutes. At this stage the reaction mixture analyses at 37.1% total isocyanate groups and consists essentially of the urethane diisocyanate formed by reaction of 2 molecules of hexamethylene diisocyanate and 1 molecule of diethylene glycol in excess hexamethylene diisocyanate.

30 The reaction mixture is then heated to 130°—135°C. and maintained at this temperature for 24 hours, by which time the total NCO value had fallen to 30.1% (theoretical value, 30.2%). A dry nitrogen atmosphere is maintained throughout the reaction.

35 Unreacted hexamethylene diisocyanate is then removed as follows. 483.5 parts of the reaction mixture is stripped of unreacted hexamethylene diisocyanate by distillation at 100°C. and a pressure of 1.4 mm. abs. using a thin film distillation apparatus. The non-volatile portion of the reaction mixture (264.7 parts) is a slightly viscous liquid analysing at 17.1% total isocyanate groups

40 and less than 0.1% unreacted hexamethylene diisocyanate. It is essentially an allophanate polyisocyanate resulting from the reaction of one molecule of hexamethylene diisocyanate with each urethane group present in the hexamethylene diisocyanate/diethylene glycol urethane diisocyanate formed in the early part of the reaction. The volatile portion (216.2 parts) is essentially hexamethylene diisocyanate. It can be reused in the process.

#### EXAMPLE 2

45 To 464 parts of 2:4-tolylene diisocyanate maintained at 70—75°C. is added over 49 minutes with stirring 35.34 parts of diethylene glycol. After completion of the addition the mixture is stirred a further hour. At this stage the mixture analyses at 38.75% total isocyanate groups and consists essentially of a solution of a urethane diisocyanate formed by reaction of 2 molecules of tolylene diisocyanate and 1 molecule of diethylene glycol in excess tolylene diisocyanate.

50 The reaction mixture is then heated to 125°C. and maintained at 125—130°C. for 19 hours by which time the total NCO value has fallen to 33.6% (theoretical value, 33.6%). A dry nitrogen atmosphere is maintained throughout the reaction.

55 Unreacted tolylene diisocyanate is then removed by extraction with petrol (boiling range 160°—120°C.) in a continuous extraction apparatus. The extracted product, essentially an allophanate polyisocyanate produced by further reaction of tolylene diisocyanate with the urethane diisocyanate formed in the early stages, from 1 molecule diethylene glycol and 2 molecules of tolylene diisocyanates, was transferred to a distillation flask and heated to 110°C. at 0.1 mm. of mercury abs. to remove residual petrol and then dissolved in sufficient butyl acetate to make a 75 solution. The final product a viscous yellow solution had a total isocyanate value of 13.51% and contained only traces of unreacted tolylene diisocyanate.

#### EXAMPLE 3

60 To 1500 parts of tolylene diisocyanate (an 80/20 mixture of the 2:4 and 2:6 isomers) maintained at 70—75°C. is added over 55 minutes 96.3 parts of molten trimethylolpropane. After completion of the addition the mixture is stirred a further hour at 70—75°C. The mixture at this stage is essentially a solution of a urethane triisocyanate formed by reaction of 3 molecules of tolylene diisocyanate with 1 molecule of trimethylolpropane in excess tolylene diisocyanate.

65 The reaction mixture is then cooled to 50°C. and 4.16 parts of a white spirit solution of zinc naphthenate added and the mixture stirred at 45—55°C. for 80 hours. The catalyst was then deactivated by the addition of 7.67 parts of a 4% solution of phosphoric

acid in ethyl acetate followed by stirring for a further 1½ hours. At this stage the product, a slightly turbid yellow solution, analysed at 34.4% total isocyanate (theoretical value, 33.7%) and contained 49.3% free unreacted tolylene diisocyanate.

#### EXAMPLE 4

To 336 parts of hexamethylene diisocyanate maintained at 70–75°C. is added over 1 hour with stirring 100 parts of oxypropylated sorbitol having a hydroxy value of 8.5%. After completion of the addition the mixture is stirred a further hour at 70–75°C. and then cooled to room temperature. At this stage the reaction mixture consists essentially of a solution of the urethane polyisocyanate formed by reaction of 6 molecules of hexamethylene diisocyanate with 1 molecule of oxypropylated sorbitol in excess hexamethylene diisocyanate.

1.09 parts of pyrrolizidine is then added and the mixture stirred at room temperature for 69 hours by which time the total isocyanate value of the mixture was 36.26% (theoretical value, 28.9%). The catalyst was then deactivated by the addition of 7.74 parts of a 4% solution of phosphoric acid in ethyl acetate followed by stirring at room temperature for 1½ hours.

The turbid pale yellow reaction mixture was then filtered through a sintered glass funnel dressed with filtercel and the unreacted hexamethylene diisocyanate removed by distillation at 100°C. and 1.4 mm Hg abs. in a thin film distillation apparatus. From 354 parts of the reaction mixture was obtained 159.6 parts of a viscous slightly turbid yellow liquid analysing at 11.2% total isocyanate group and less than 0.5% free hexamethylene diisocyanate. 180.5 parts of unreacted hexamethylene diisocyanate was recovered.

#### EXAMPLE 5

To 336 parts of hexamethylene diisocyanate maintained at 70–75°C. is added over 1 hour with stirring 100 parts of oxypropylated sorbitol having an OH value of 8.5%. After completion of the addition the mixture is stirred a further 2½ hours at 70–75°C. At this stage the reaction mixture consists essentially of a solution of the urethane polyisocyanate formed by reaction of 6 molecules of hexamethylene diisocyanate with 1 molecule of oxypropylated sorbitol in excess hexamethylene diisocyanate.

To this solution of urethane polyisocyanate in excess diisocyanate is then added 2.27 parts of a white spirit solution of zinc naphthenate and the mixture then stirred at room temperature for 69 hours by which time the total NCO value is 30.1% (theoretical value, 28.9%). The catalyst is then deactivated by the addition of 4.24 parts of a 4% solution of phosphoric acid in ethyl acetate

followed by stirring at room temperature for 1½ hours.

Unreacted hexamethylene diisocyanate is then removed. 396 parts of the clear pale yellow liquid reaction mixture is passed down an agitated thin film distillation apparatus at a temperature of 100°C. and a pressure of 1.3–1.9 mm. Hg. abs. The non-volatile portion of the reaction mixture (188.9 parts) is a clear pale viscous liquid analysing at 11.34% total isocyanate groups, and less than 0.5% free hexamethylene diisocyanate. It is essentially an allophanate polyisocyanate produced by reaction of hexamethylene diisocyanate with the hexamethylene diisocyanate/oxypropylated sorbitol urethane polyisocyanate formed in the early part of the reaction. The volatile portion (198.5 parts) is essentially hexamethylene diisocyanate. It can be reused in the process.

#### EXAMPLE 6

Tolyene diisocyanate (1531.2 parts of an 80/20 mixture of 2:4 and 2:6 isomers) is stirred and heated to 70°C. under a dry nitrogen atmosphere and molten trimethylol propane (96.3 parts) added dropwise over 55 minutes, the internal temperature being maintained at 70–75°C. When the addition of the polyol is complete, the temperature is maintained at 70–75°C. for a further hour. The product at this stage, a solution of urethane polyisocyanate in excess tolylene diisocyanate analyses at 39.1% total isocyanate groups.

The reaction mixture is then heated with stirring to an internal temperature of 130–135°C. for a further period of 41 hours by which time the total NCO value of the mixture has fallen to 34.4% (theoretical value, 33.7%).

#### EXAMPLE 7

Into 100 parts of the liquid polyether prepared by adding propylene oxide to triethanolamine to give a product of hydroxyl value 445 mgs. KOH/g. and viscosity 3.3 poises at 25°C. are stirred 30 parts of tri-*β*-chloroethyl phosphate, 6 parts of water, 12 parts of triethanolamine and 4 parts of a polypropylene/polyethylene oxide block copolymer of MW 2,000 containing 10% polyethylene oxide.

When the above mixture is homogeneous, 270 parts of the product of Example 6 are added and the whole is given a vigorous stirring for 10 seconds, expansion occurs over the following 30 seconds to yield a fine textured cellular rigid product of density 1.9 lb./cu.ft.

This example illustrates the use of a product of the invention in the manufacture of a cellular polyurethane product.

#### EXAMPLE 8

The product of Example 5 (40 parts) is

mixed with dry ethylene glycol monoethyl ether acetate (60 parts) and 0.3 parts dibutyl tin dilaurate and the solution painted on to clean tinned iron plates.

- 5 After standing overnight a film having good adhesion and resistance to chemicals is obtained.

A film having similar properties was also obtained by stoving the film in a moist atmosphere at 120°C. for 30 minutes. The films were resistant to U.V. light and showed no yellowing after exposure to U.V. light for several hours.

- 10 This example illustrates the use of the products of this invention in the manufacture of surface coatings.

#### WHAT WE CLAIM IS:—

1. Compositions of matter consisting essentially of allophanate polyisocyanates, which compositions are obtainable by reacting an amount in excess of  $n$  moles of an organic diisocyanate with one mole of a urethane isocyanate of the general formula  $R'(OOCNHRNCO)_n$ , wherein  $R'$  is a monovalent or polyvalent organic radical which is the residue of a mono- or polyhydroxylic compound after reaction of the hydroxyl groups with isocyanate groups,  $n$  is an integer from 1 to 6 and represents the functionality of the hydroxylic compound and  $R$  is a divalent substituted or unsubstituted organic radical, the reaction being carried out under conditions such that substantially one molecule of diisocyanate reacts with each urethane group present, as indicated by the measured isocyanate group content of the reaction mixture.

2. Products as claimed in Claim 1 wherein  $R$  is a divalent radical derived from toluene, hexane, benzene, xylene or methyl cyclohexane.

3. Products as claimed in Claim 1 wherein

$R'$  is the residue of a polyhydroxy compound having from 2 to 6 hydroxy groups.

4. Products as claimed in Claim 1 wherein the organic diisocyanate is hexamethylene diisocyanate, a tolylene diisocyanate a methylcyclohexyl diisocyanate or a xylylene diisocyanate.

5. Process for the preparation of the products claimed in Claim 1 comprising reacting an excess of organic diisocyanate with a urethane isocyanate as hereinbefore defined.

6. Process as claimed in Claim 5 wherein there is incorporated as catalyst, a metal carboxylate, a metal chelate or a tertiary amine.

7. Process as claimed in Claim 5 wherein the excess of organic diisocyanate is from 10% to 300% over that required for the reaction of one molecule of diisocyanate with each urethane group.

8. Process for the manufacture of homogeneous or cellular, rigid or flexible polyurethane products, characterised in that as polyisocyanate in such manufacture, there is used a product as claimed in Claim 1.

9. Process as claimed in Claim 8 wherein the polyurethane product is in the form of a coating composition.

10. Product as claimed in Claim 1, substantially as hereinbefore described, especially with reference to Examples 1 to 6.

11. Process for the manufacture of polyurethane products as claimed in Claims 8 or 9 substantially as hereinbefore described, especially with reference to Examples 7 and 8.

12. Polyurethane products whenever manufactured by a process as claimed in Claim 8.

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